A LIQUEFACTION KINETIC RESEARCH NEEDS ASSESSMENT

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INTRODUCTION In February 1989, the Department of Energy released its assessment of the research needs for coal liquefaction.[1] Under direct liquefaction, 4 of the 12 recommendations focused on developing models and determining kinetics. Reasons accompanying these recommendations stressed the need to understand the retrograde reactions, the reactions taking place as the coal is heated to the reaction temperature, and the effects of coal types and solvent on liquefaction reactions. By understanding the liquefaction process better, suggestions for improving the process may be made. A good kinetic model would provide a basis for testing suggestions which would attempt to control reactions or effects in the development of improved liquefaction technologies. Brandes et al. suggests that a kinetic model could also possibly have a large impact on the economics of coal liquefaction.[2] Cost factors which could be studied using a kinetic model include: coal preparations, reactor throughput, hydrogen usage, catalyst usage, product yields and selectivity, and process control.

The purpose then of a kinetic model is to have a tool for evaluating the liquefaction process as the inputs and the processing conditions are changed. The model has to be able to account for the effects of these changes and provide valuable results to someone using the model. As a starting point for the development of this type of kinetic model, the assessment described in this work was carried out. The assessment included an intense review of earlier kinetic models found in the literature, along with reviews of the current work being carried out in this area. It was meant to discover the strengths, weaknesses, and limitations of available models and provide guidelines for future models. At the same time, the assessment looked at questions of who uses liquefaction models, why they use them, and what they expect the model to do.

SMALL-SCALE MODELS At the level of small-scale processes, most kinetic models for batch reactors use a variation on the simplified reaction scheme shown in Figure 1. Reaction rate constants are determined in each of these studies by fitting liquefaction results obtained in that particular set of experiments. Because of this, no consistent set of rate constants or activation energies has been found for these reactions. Even within a single study, changing coal or solvents required new rate constants to be determined. More complicated reaction schemes, based more on the actual chemistry taking place during the liquefaction process, have also been developed. A scheme by Suzuki, shown in Figure 2, includes a free radical pool as the first product of coal dissolution.[3] This allows retrograde reactions to be included as one of the important reactions taking place during liquefaction.

Weller found four problems with these types of kinetic models.[4] First, the reactions listed are not elementary and therefore cannot be described by simple rate laws. Second, the liquefaction system is not a single phase. Third, the quantities used in rate laws must be described in terms of liquid-phase concentration, not just masses in the reactor. Fourth, the reactivity of the intermediate products change with time. This assessment has revealed three additional problems with these models. One, they do not include hydrogen as a reactant but assume hydrogen is present in excess and does not affect the rates. Two, reactions during heat-up times are usually ignored, but even for fast heat-ups (1-2 min) significant amounts of the coal will break down during this period. Three, these models do not fulfill the basic purpose of a model because they have little predictive value for determining results of liquefactions run under different processing conditions.

This situation has been partially corrected in a current model containing additional retrograde reactions and calculations during the heat-up time.[5] The reaction scheme for this model is shown in Figure 3. The kinetic expressions derived from this scheme are based not on mass, but on liquid-phase concentrations. This can be done because thermodynamic calculations are also included in the model to account for the three-phase nature of the liquefaction process. Hydrogen is included directly in the necessary expressions, and the gas-phase contribution to this concentration is determined through the mass transport calculations which are also part of the model. Processing variables are incorporated directly into these calculations in one or more ways. An example is the type of solvent, which affects mass transport through its viscosity, thermodynamics through its partition coefficient, and kinetics through its hydrogen donating ability. The effects of changing some processing variables can be predicted, but some important variables, such as the type of catalyst used, have not yet been incorporated into this model.

Like most of the earlier models, this model also suffers from the fact that the reactions are not truly elementary and the reactivity of the intermediate products change. Lack of

elementary reactions in the scheme is inherent in any model dealing with coal. Because of the large number of reactions actually taking place within the coal, there is no real way to include and write kinetic expressions for all of these reactions (see Current Models below). In models which lump the products as preasphaltenes, asphaltenes, and oils, these simple product definitions give no indication of the internal nature of each product. Reactions within a single product, which change the quality and reactivity of that product, cannot be included in the model. Inclusion of more product fractions in the model would be one way of handling this problem. The small amounts of material recovered in small-scale batch reactors, however, often prevent further fractionation of the products.

In continuous reactors, sufficient product can be recovered for separation into additional fractions, but this is not always done. Many of the models for continuous reactors therefore also use solubility-defined products and suffer from the same problems as the batch models. Studies which have fractionated the oil into more species by boiling point ranges usually then lump the widely different preasphaltene, asphaltene, and nondistillable oil fractions as a single fraction. This single product is usually called resid or solvent refined coal (SRC). Though reactions and reactivities of the distillate fractions can be defined in models using such products, the major changes which take place within the resid product are now lost.

One of the better continuous models was given by Singh et al.[6] This model defined three distillate products based on boiling point ranges along with a SRC product. The kinetic expressions developed in the model included terms for both the hydrogen pressure and the mineral matter content of the slurry. Inclusion of these terms made the model applicable to more situations, but no justification was given as to the final form of these terms which were based on empirical fitting of experimental data. In addition, the kinetic parameters were still limited by a simplified reaction scheme, containing an instantaneous initial reaction and no retrograde reactions and experimental data from only a single coal.

LARGER SCALE MODELS Kinetic modeling of large-scale liquefaction processes was carried out using both Wilsonville and HTI pilot plant data. The Wilsonville model was developed in two parts using data from both the actual plant and a specially designed batch reactor.[7] For the thermal liquefaction unit, the reaction scheme, shown in Figure 4, considered light and heavy hydrocarbon gas products along with a resid fraction, but lumped all of the liquid product into a single distillate fraction. Heteroatom gases were also included as products since much of the hydrogen used in the liquefaction process goes into these products. In setting up the actual kinetic expressions, the Wilsonville model developers used the results of tracer studies which showed that the thermal liquefaction unit could be modeled as a CSTR. However, two different residence time definitions were used in the various kinetic expressions. The actual residence time above 370°C, including both the reactor and part of the preheater, was used in the hydrocarbon gas formation expressions, but the nominal residence time, just over the reactor, was used in the heteroatom expressions. These choices came purely from data fitting and had no theoretical basis.

The hydrotreating unit part of the Wilsonville model included a set of secondary reactions considered to be purely catalytic. These reactions, shown in Figure 5, included hydrotreated resid and hydrotreated distillate products. Internal reactions within these two products are included in the model to account for changes in their reactivity and composition. No indication was given, however, on how these hydrotreated products could be separated or identified, and kinetic expressions were not developed for these reactions. Catalyst deactivation terms were included in the kinetic expressions which were determined from this reaction scheme.

The overall Wilsonville model was thus not only specific for the processing condition being used, but suffered from the same problems as the small-scale models. Two-phase effects were accounted for in some of the expressions by using actual residence times, but not for all of the reactions, and the choice of residence time definition for a reaction was not justified. The reaction scheme was also too simplified with product lumps which were too encompassing.

The model developed at HTI, shown in Figure 6, is significantly different from the Wilsonville model.[8] Two distillate products, a high boiling gas-oil, and a low boiling naphtha, were defined, along with resid and gaseous products. High, low, and unreactive coal fractions were defined, and the reactions scheme included both parallel and implied sequential reaction pathways leading from coal to all of the products. This represents a move towards a reaction scheme based more on the underlying liquefaction mechanisms. Two problems remain, however. First, there are no retrograde reactions specified, and, second, no secondary reaction scheme is established.

Coal type was taken into account in the model by the amounts of high, low, and unreactive fractions (a, b, and c), and by the distribution of products formed in the initial parallel reactions during coal dissolution (f-j). One would then expect that if a-c and f-j could be determined independent of the model, then liquefaction using any coal type could be predicted by this model. Unfortunately, the rate constants (k_1 and k_2) used in the coal breakdown reactions were also made coal dependent. Catalyst deactivation rates, included for reactions which were

found to be catalyst dependent, were made coal dependent as well.

Additional problems with the HTI model included inconsistencies in both the reaction scheme and the rate constants which required changes in the model when it was applied to batch autoclave liquefactions. The model developers suggest that their product lumps are too large and that significant changes occur within the individual product fractions during liquefaction. No reactions describing this process are included in the model, however. There are no kinetic expressions for heteroatom removal or hydrogen consumption, and gas-oil kinetics are only found by difference in the model rather than through a direct expression.

CURRENT WORK In addition to the current model for small-scale batch processes described above,[5] work is also being conducted on statistical models. These models represent coal by a large number of random chain molecules which have the same statistical characteristics (carbon content, aromatic content, etc,) as the original coal. Rules for breaking bonds within the chains are specified and a Monte Carlo simulation is run to follow the breakdown of the coal molecules with time. By defining products based on specific chain characteristics, the production of individual products with time can also be followed. To be comparable to experimental data, the products defined in the model must be characterizable by methods currently available for analyzing coal liquefaction products.

Monte Carlo simulations require significant amounts of computer time to carry out. This time increases greatly as the number of initial molecules in the simulation increases, as the number of possible reactions increase, or as simulation time is increased. This limits the starting point to a small representative sample of all possible coal chain molecules. Reactions which take place within a single product fraction, such as naphtha, can be included, but will not really be detectable at the actual experimental level. In addition, these simulations usually represent purely kinetic descriptions of the process and do not account for transport or thermodynamic considerations of the reaction system.

MODEL USERS Two groups of researchers are expected to be the predominant users of coal liquefaction kinetic models: those who use them for economic analysis, and those who use them for scientific or engineering analysis. For economic analysis of large-scale processes, the structure or organization of the model itself is not usually important. What is needed is for the model to accept specific characteristics of input streams and predict the expected compositions of the output streams. If the type of reactor and separation units to be used are known, cost analysis will focus mainly on changes in the amounts of useful product in the exit stream as processing conditions are changed. Catalyst cost is a major factor, however, so both economic and scientific users are interested in the rate at which catalyst must be replaced in the reactor.

Scientific users are more interested in what is going on inside the reactor and how various conditions affect the process. The model must be able to show what happens as the space velocity is changed, as the reactor temperature is changed, or as the hydrogen treat rate is changed. It would be beneficial to separate the kinetics of the reactions from the physical effects of the reactor, such that the model is applicable to any reactor system design. By having an accurate description of what is going on inside the reactor, it may also be possible to adjust conditions to control the particular reactions taking place.

RESULTS This assessment has helped to identify a number of specific areas important to the development of future kinetic models. Decoupling of the processing variables from the kinetic parameters is needed to make the model applicable over a wider range of experimental conditions. To do this, intrinsic rate constants must be determined for the various reaction steps which are independent of the coal, solvent, reactor, and all other processing conditions. Since the model must still be able to predict the effects of changing these processing conditions, other ways must be found to incorporate these variables.

Some of the models described above have begun to take these variables into account, but this is only a start. In the model of Ferrance and Holder, literature correlations based on coal characteristics are used to determine ultimate conversions and hydrogen availability.[5] These correlations, however, were developed using data from a limited range of coals. More basic research is needed to extend the applicability of such correlations to the entire range of coal types. Similar correlations, independent of the model itself, will also be needed to determine initial product distributions and the hydrogen donating ability of both coals and solvents.

Decoupling the reaction rates from the design of the reactor will make the kinetics applicable to all reactor setups. This means that the model will have to be able to handle and incorporate the mixing and mass transport characteristics within the reactor. Mass transport calculations will require accurate predictions of the viscosity and hydrogen gas solubility of the slurry, two areas in which further work needs to be carried out. In addition to solubilities, other areas of the thermodynamics of liquefaction systems also need work. In particular, studies are needed on partitioning of the solvent and light products into the vapor-phase since these may represent the hydrogen donating or hydrogen shuttling species in the reactor.

While modeling of both small-scale and large-scale reactors would be possible, much more work is needed for development of a large-scale model which can be used for both economic and engineering purposes on a commercial level. For work at this scale, inclusion of the preheater in the model was determined to be of great importance. Simulation of pilot plant preheaters have shown that up to 90% of the total coal conversion may be complete by the time the slurry exits the preheater.[9] The rates of the coal dissolution reactions are very fast and produce large changes in the characteristics of the slurry. Free radical and retrograde reactions which occur as the slurry is heated may have an influence on the final product yields. The possible presence now of dispersed catalyst in the preheater, fed or recycled with the slurry, adds to the complexity of the reactions occurring in this unit.

Product definitions have also been found to be an important area in which improvements are needed, because the reaction scheme and kinetic expressions depend on the products. What is needed, is standardization of a choice of product fractions which can be analytically defined and experimentally characterized. For the distillate products, definition of fractions by boiling point ranges will allow use of the various correlations developed by the petroleum industry. For the nondistillable products, additional solubility separations might be possible, or molecular weight separations might be used to give additional fractions. CONSOL has directed a study to evaluate the usefulness of various analytical methods for characterizing coal liquefaction process streams.[10] Though applicable methods have been determined, no set of products which could be defined by these methods has been established.

Enough product fractions must be defined so that each fraction has stable and consistent physical and thermodynamic properties which can be used for engineering analyses. Inclusion of too many product fractions, however, will lead to a large number of reactions and an unwieldy model. A reaction scheme will have to be set up relating how each of these products, plus any additional intermediates are formed and reacted. The scheme must include a set of initial reactions, giving the products formed directly from the coal, as well as a set of secondary reactions describing the further breakdown into low molecular weight products. As this reaction scheme is setup, it is also important to distinguish between those reactions which are purely thermal, those which have both thermal and catalytic components, and those which are only catalytic. The assessment has found that this is the best way to explicitly include the impact of catalysts in the model. Rate constants for the catalytic reactions will always be catalyst dependent and will have to be determined independently for each catalyst. However, incorporation of catalyst variables, such as the amount of catalyst or the catalyst particle size, must be independent of these rate constants for the model to be valuable.

EXPERIMENTAL Experimental work has begun at the Pittsburgh Energy Technology Center in conjunction with the assessment to study some of these areas. Determining a workable reaction scheme was felt to be the most important contribution at this stage. To do this, specific product cuts from a bench-scale continuous facility are being reacted in microautoclave reactors under different conditions. Both the initial and reacted products are being analyzed to determine how fractions can be defined using readily available techniques. How the amounts and types of fractions change during the process will help to elucidate the secondary reactions which take place during liquefaction to convert or produce each fraction.

A second set of experiments has been designed to investigate the initial reactions which take place. In these experiments, coal will be reacted in microautoclave reactors under conditions typically found in a coal liquefaction preheater. Time/temperature profiles determined for pilot-plant preheaters are shown in Figure 7.[11-12] By simulating heating of the coal to different temperatures along this curve in a tubing bomb, the initial reactions which occur as coal is converted to a liquid will be observed. The prevalence of secondary reactions taking place before the slurry exits the preheater will also be determined through these experiments. A true scheme for the formation of light products from coal both directly and through sequential reactions will be developed. This determination of the early reactions taking place in the preheater should help in the design of better preheaters for large-scale processes.

FUTURE WORK The assessment is not complete. Discussions with investigators working at both the bench-scale and larger scale continue to provide additional input on what should be incorporated into future models to make them useful and valuable. This input is solicited through distribution of preliminary reports and on-line through a coal liquefaction kinetic modeling home page (http://www.petc.doe.gov/kinetics.html).

What has become evident already is that kinetic modeling has developed independent of mass transport and thermodynamic considerations which affect the liquefaction process. Future efforts will require assessing the studies carried out in these areas to determine what additional work will be needed to incorporate these results into liquefaction models. Monitoring of current external experimental work relevant to all areas listed will continue. Continuing adjustments of the PETC internal experimental program as data is collected, and as additional input arrives will also be carried out.

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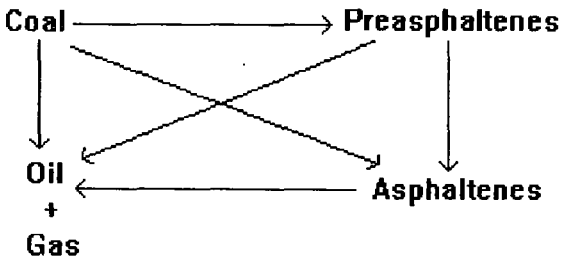

Figure 1 Reaction scheme used in most earlier simple models

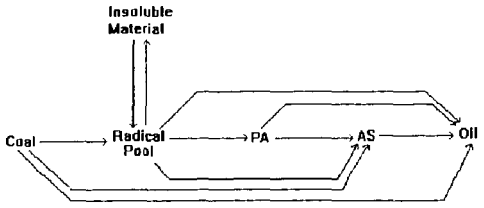

Figure 2 Reaction scheme of a recent model by Suzuki.

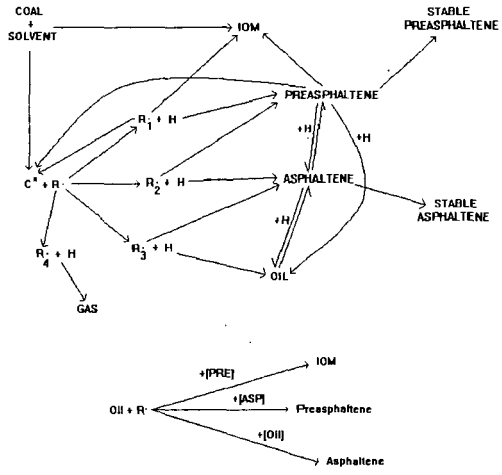

Figure 3 Reaction scheme of Ferrance and Holder

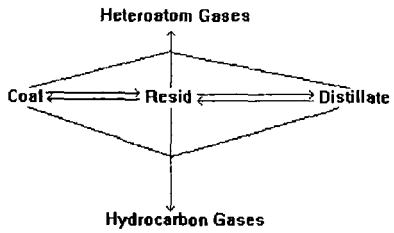

Figure 4 Wilsonville reaction scheme for the thermal liquefaction unit

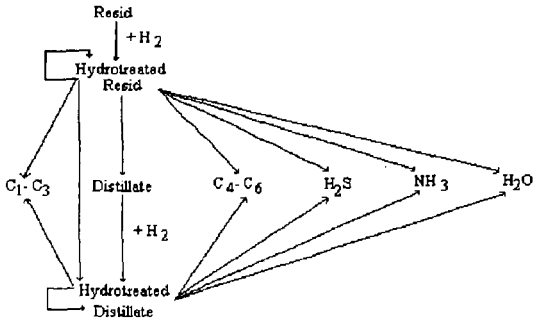

Figure 5 Wilsonville reaction scheme for the hydrotreater unit

$$Coal \xrightarrow{\qquad\qquad} a\,C_1 + b\,C_2 + c\,Unreactive\ Coal$$

$$C_1 \xrightarrow{k_1} f Resid + g Gas\ oil + h Naphtha + i Hydrocarbon\ gases + j Byproduct\ gases$$

$$C_2 \xrightarrow{k_2} f Resid + g Gas\ oil + h Naphtha + i Hydrocarbon\ gases + j Byproduct\ gases$$

$$Resid + H_2 \xrightarrow{catalyst} Products$$

Figure 6 Reactions used in the HTI coal liquefaction model

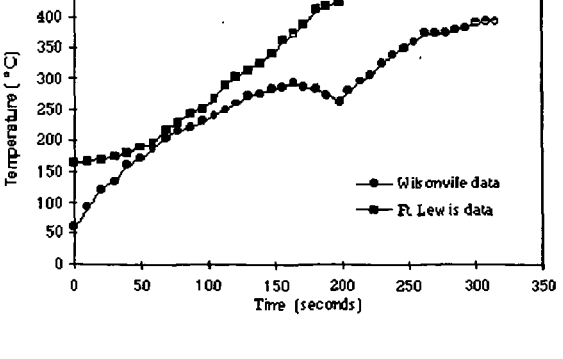

Figure 7 Time/temperature profiles for two pilot-plant preheaters